The Potential VOC Offset by Carbon Monoxide Reduction

by

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This paper updates a previous analysis (Whitten, 2005) of the carbon monoxide (CO)-related VOC offset built into the California RFG regulations. This new offset amounts to 72 tons per day of on-road VOC equivalents from using E10 compared to non-oxy fuel or E0; consideration of non-road impacts could add another 19 tons per day to this bringing the total to about 90 tons per day VOC equivalents. In terms of grams per on-road gasoline vehicle the CO reduction calculated here is 105 grams per day for E10 and 60 grams per day for E5.7, which compares to a recent ARB estimate of only 7.8 grams per day of CO for E5.7. The net balance between these offsets and ethanol-related permeation emissions continues to be an issue (along with a NOx issue discussed below) in the current plans to modify these RFG regulations.

As the present regulations for Phase 3 of the California RFG program were finalized, a concern over increased permeation emissions of volatile organic compounds (VOC) due to the use of ethanol lead to the creation of an offset between CO and any anticipated permeation increases from its use in CaRFG3. The form of this "offset" was to not debit non-oxygenated CaRFG3 for increases of CO over the base "flatline" CaRFG3, which contains 2 weight-percent oxygen.

The ARB (2000) stated;

"Moreover, a gasoline with zero oxygen will have lower rates of permeation emissions than fuels with ethanol or MTBE. The lower permeation emissions from gasoline with no oxygen appear to more than offset the increase in ozone-forming potential from the higher CO emissions. Thus, it is not necessary to include a CO debit mechanism in the final regulations."

Along with banning MTBE, CaRF3 was designed to give increased flexibility for the use of 100% petroleum non-oxygenated fuel.

Background

Fuel oxygen is well-known to reduce tailpipe CO emissions and CO is a well-known VOC-like precursor to ozone formation (National Academy, 1999). Although CO is a VOC-like ozone precursor, on a weight basis CO is significantly less reactive towards forming ozone than typical mobile-related VOC. However, the amount of CO emitted by gasoline-burning vehicles is significantly more than the total VOC emissions. The

National Academy (1999) estimated that "CO in exhaust emissions from motor vehicles contributes about 20% to the overall [ozone-forming] reactivity of motor-vehicle emissions." The National Academy (1999) also recommended that potential variations in CO emissions be accounted for in RFG programs. Both the U.S. EPA (66 **FR** 37156, 17 July, 2001) and the California Air Resources Board in its CaRFG3 regulations have followed this recommendation for cases involving fuel oxygen over the base of 2 weight percent.

In the CaRFG3 regulations fuels with oxygen above the base "flatline" value of 2 percent a VOC credit is assigned for CO reduction through the use of a reactivity factor that gives 0.021 VOC weight "credit" for each weight unit of CO reduced by the fuel oxygen over the 2 percent (required) oxygen base. The 0.021 value is the ratio of MIR reactivity factors for CO and exhaust VOC that were developed by W.P.L. Carter (1994) using a single-day single-cell box model for 1-hour ozone under non-SIP conditions. The CO-reduction credit is derived from an assumed CO to VOC emissions ratio and an existing (see below) 5.9 percent reduction of carbon monoxide emissions per weight percent of fuel oxygen. Thus, for example a fuel with 3.5 weight percent oxygen could get some VOC credit that might be used to offset say some of the volatility increase caused by blending with ethanol. However, for fuels with oxygen content less than the base of 2 percent there is no VOC or other debit assigned for the increases in CO that can occur due to less fuel oxygen than 2 percent which forms the basis (for regulatory emissions comparison) of CaRFG3 gasoline. As noted above the ARB has stated that the reason for this lack of debit was to encourage the use of non-oxygenated CaRFG3 because the use of ethanol could lead to (then unknown) increases in VOC emissions due to permeation from fuel containers, seals, and hoses.

Recent Developments

Although it has been over a year since the Coordinating Research Council released its E-65 study of ethanol-enhanced permeation emissions, estimates of the daily tons of VOC released in California due to ethanol use are still under investigation. Therefore, this present CO offset analysis will not be quoting any draft estimates of permeation.

On one hand, the MIR factors have been updated (Carter, 2005) from those now used in CaRFG3 so that the original 0.021 CO to exhaust VOC reactivity ratio might be reduced to only 0.017. On the other hand, the ARB is now considering the use of multi-day multi-cell grid-models and 8-hour ozone values under SIP-like conditions to evaluate reactivity factors and that current estimate implies a higher reactivity ratio of 0.026 for CO to exhaust VOC (Luo, 2006). Although higher the MIR factors used previously, this new ARB estimate is still less than other estimates based on total VOCs rather than exhaust such as the U.S. EPA estimate of 0.067 (66 **FR** 37156, 17 July, 2001) or especially a 2002 European estimate as high as 0.11[1].

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[1] See http://themes.eea.eu.int/IMS/ISpecs/ISpecification20041001123013/guide_summary_plus_public?printable=yesDefinition

Other developments (described in detail below) associated with the CO offset concern the percent reduction of carbon monoxide emissions per weight percent of fuel oxygen. The original 5.9333 value built into the present Predictive Model was derived based on a combination emissions inventory estimates available in 2001 for the various technology classes and on estimates of the percentage CO reductions from oxygenated fuel for these same various technology classes. Due to a lack of data an assumption was made for vehicles built after 1995 (Tech 5) such that these vehicles would have zero CO reduction from using oxygenated gasoline. Studies by Alliance (2001) and CRC-67 (2006) show that significant CO reductions are possible from fuels containing oxygen. Also the ARB continues to update emissions inventories and the most recent inventory implies more CO emissions in California than estimated when the Predictive Model was created.

Finally, there is some evidence that suggests that the ratio of CO emissions to exhaust VOC emissions may need further refinement in the ARB inventories.

Without considering any refinement to the ARB estimate for the ratio of CO emissions the other recent developments alone lead to a new estimate of 70 tons VOC equivalent per day offset by E10 reductions in CO compared to E0 fuels for 2005 (the base year used for CaRFG3); and the non-road impacts could add another 20 tons per day to this bringing the total offset to about 90 tons per day VOC equivalents.

Detailed Analyses

The Reduction in CO Due to Fuel Oxygen --- As noted above, a permeation offset was originally built into the CaRFG3 regulations as described in Appendix G, of the 22 October, 1999, "Staff Report: Initial Statement of reasons, for the Proposed California Phase 3 Reformulated Gasoline Regulations." The full Appendix G is reprinted here as Attachment A. Two key assumptions in this Appendix G are contrary to well documented recommendations and recent data. One of these assumptions was that the CO impact from fuel oxygen is abruptly non-linear at 2 weight percent oxygen such that the CO reduction below 2 percent oxygen is much less than above (See Attachment A, page G7). Second, it was assumed in this Appendix G that the vehicles from model year 1995 to present (Tech 5) have zero CO reduction from fuel oxygen (See Attachment A, Tables 4 and 5, page G3). These assumptions are challenged as follows:

>Non-linear CO response with fuel oxygen – This issue was addressed in the OSTP (1997) study. In that study, a blue-ribbon panel of scientists concluded that the response of vehicles to fuel oxygen should be considered linear because all the CO reduction data was presented on the basis of a percentage CO reduction per percent weight fuel oxygen. The ARB has not supplied evidence to support the use of a non-linear relationship between fuel oxygen and CO reductions. Actually, the ARB itself assumed a linear relationship especially between zero and 2.7 weight percent fuel oxygen when the ARB applied for a waiver to use only 2 (instead of the required 2.7) weight

percent oxygen in its wintertime oxygenates program. In ARB Final Statement of Reasons (September, 1992) the ARB stated:

"The adopted wintertime oxygenates regulation will achieve most of the CO reductions that would result under the full federal program. The staff estimates that the regulation adopted by the Board will reduce CO emissions from gasoline vehicles by about 10 percent. In comparison, adoption of the federal program would result in a CO emissions decrease of about 13 percent.[2]"

In the Appendix G discussion shown below in Attachment A, it is noted that a large part of the CO impact above 2 weight percent is based on data that includes aggressive driving (REP05), but no data was available at that time to show a significant CO response to fuel oxygen below 2 weight percent[3]. There now exist data that may show impacts between zero, 2, and 3.5 weight percent oxygen. Such data were taken as part of an Alliance study "performed at the request of CARB in conjunction with the MTBE-ban and new CBF3 [CaRFG] regulations." Although the bulk of the data from the Alliance study were released by July, 2001, (the fuel oxygen data were too late to become part of the CaRFG3 regulations) the aggressive driving data (US06) has still yet to be released. Perhaps, since the Alliance study was "performed at the request of CARB," the ARB might be more successful than this author in obtaining the Alliance US06 data.

In response to questions on CaRFG3 the California ARB has alluded to a belief that the CO reduction below 2 weight percent fuel oxygen would be non-linear and less due to T-50 and sulfur reductions used by refiners to meet the NMOG requirements for non-oxygen CaRFG3. Appendix G (reproduced in Attachment A below) discusses this also. As noted above, the ARB staff have yet to supply evidence to support their T-50 and sulfur claims. On the contrary, data on recent non-oxygenated CaRFG3 fuels have been supplied to this author by the ARB that refute this claim.

During 2003 there were at least 3 refineries supplying non-oxygenated CaRFG3 gasoline in California. In 2004 data from only one refiner was available from the ARB. Apparently, non-oxy CaRFG3 was more widely in use during 2003.

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[2] Actually, the 1994 Caldecott Tunnel data published by Kirchstetter et al. (1996) showed that CO was reduced by 21 percent in spite of increased sulfur in the oxygenated gasoline. Also Whitten and Cohen (1996) showed on average at over 300 sites nationally that the federal program achieved a 14 percent CO reduction.

[3] It is also curious, as shown in Table 5, page G3 of Attachment A, that the ARB was willing to apply the aggressive driving credit to all model-year vehicle-groups in spite of data not available for all these categories. Yet the ARB used the "no data" reason to abruptly diminish CO response to fuel oxygen for fuels with less than 2 weight percent.

California Air Resources Board -- Enforcement Division Test Results
Non-Oxy Gasoline from Northern California Refineries for 2003 and 2004.

Date sampled	Refinery	Grade	Benzene v%	Aromatics v%	Olefin v%	T50	T90	Sulfur ppm	RVP
April 2004	1	Regular	0.31	22.1	9.4	210	303	6	6.66
April 2004	1	Premium	0.20	23.6	9.1	212	305	5	6.54
April 2004	1	Premium	0.20	23.5	9.1	212	305	5	6.56
July 2004	1	Regular	0.24	23.2	7.5	211	307	4	6.70
July 2004	1	Premium	0.37	23.7	7.2	211	307	5	6.67
Dec – 2004	1	Regular	0.27	18.5	10.5	210	308	5	no test
Sept – 2003	1	Regular	0.40	23.0	9.5	206	302	6	6.58
Sept – 2003	1	Premium	0.25	24.0	9.2	207	309	5	6.74
Sept – 2003	1	Regular	0.39	23.1	9.2	207	300	5	6.60
Sept – 2003	2	Regular	0.75	29.1	0.0	207	313	3	6.63
Nov – 2003	3	Regular	0.71	28.5	3.9	193	300	12	no test
Nov – 2003	2	Premium	0.62	24.9	0.5	195	314	2	no test
Nov – 2003	2	Regular	0.27	29.0	0.4	189	311	1	no test
Nov – 2003	1	Premium	0.15	22.3	8.8	214	314	4	no test
Nov – 2003	1	Regular	0.33	21.6	7.7	211	304	6	no test

For ethanol-containing CaRFG3 a volume-weighted average fuel for 2004 is available in the AIR (2005) final report. This averaged fuel was obtained from oil industry stakeholders via E-mail from Jim Uhlein, BP, on 2 September, 2004. The properties of this fuel, with 6 percent ethanol (2.1 percent weight oxygen), are as follows:

Benzene v%	Aromatics v%	Olefin v%	T50	T90	Sulfur ppm	RVP
0.6	23.0	4.0	209	307	11	6.87

The ARB Draft Report of February, 2005, claims that "The fuel properties necessary to reduce hydrocarbons also reduce the emissions of CO. As a result, these changes significantly lessen the magnitude of any CO emissions associated with the removal of oxygen from CaRFG3, by about half …" While this claim is not clearly substantiated in the February Draft report, the ARB had previously addressed this issue in Appendix G as noted above. In this 1999 Appendix G the ARB claims that "Of the eight fuel properties that are regulated by the CaRFG2[sic] regulations, the ones that are most likely to be adjusted to offset the increase in hydrocarbon emissions would be sulfur and T50." The fuel properties shown above do not clearly support this claim. The most consistent adjustment for hydrocarbons is a reduction in RVP, which would reduce non-exhaust hydrocarbons but, at these levels of RVP, would not impact CO exhaust emissions.

A minor reduction in sulfur content is evident in the fuel properties shown above. The change to non-oxy CaRFG3 from the averaged E6 fuel with 11 ppm sulfur shows a fairly consistent reduction in sulfur of about a factor of two. Using the Predictive Model and starting with the averaged E6 fuel a reduction of only sulfur to 5.5 ppm accounts for only a 0.3 percent reduction in THC. However, Technical Bulletin No. 18 from the Auto/Oil Air Quality Improvement Research Program indicates that percentage CO reductions from fuel sulfur reductions are only about half those for THC for Tech 4 vehicles. Hence, the evidence presented here from real-world fuels shows that changes between E6 and non-oxy CaRFG3 in neither T50 nor sulfur could significantly impact the CO increases expected from non-oxy fuels in California.

> Zero Tech 5 Response -- Apart from linearity, the other issue on CO reduction to be discussed here is the assumption noted above from Appendix G, Table 5 (page G3 below in Attachment A) that vehicles since 1995 (Tech 5) would show zero reduction in CO from fuel oxygen. To address this issue, we will return to the derivation in this 1999 Appendix G for the overall fleet CO reduction of 5.9333 per weight percent of fuel oxygen as is used in the present Predictive Model[4]. In Table 5 of this Appendix G (page G3 below), the reduction from 1 percent change in fuel oxygen is estimated to be 296.44 tons per day CO. In Table 3 of this same Appendix G (page G2 below), it is shown that the emissions of CO for 2005 were estimated at that time to be 4995 tons per day in California, which implies a 5.93 percent reduction of CO for each 1 percent change in fuel oxygen. In this Table 5 the CO reduction from model years 1996 to 2005 (Tech 5) is shown to be zero for each 1 percent increase in fuel oxygen over the flatline 2 weight percent fuel oxygen.

The 2001 Alliance study shows that Tech 5 vehicles appear to reduce the CO emissions by 7.5 percent per fuel oxygen percent[5] and the Alliance study shows that the data and the regression equation giving the 7.5 percent CO reduction per percent fuel oxygen are consistent with a linear response assumption between zero and 4 weight percent fuel oxygen. Furthermore, the fuels that were used were mixed "attempting to hold key fuel parameters constant," so that the data would be most appropriate for use in the Predictive Model. However, these key Tech 5 oxy-fuel results were not available in time to be codified into the current Predictive Model (June, 2001) and so the zero impact and non-linear assumptions were used instead

In this original Table 5 of ARB's Appendix G, an attempt was made to relate FTP data to newer tests that involve aggressive driving by incorporating a factor of 2.8 into the CO reduction on top of the FTP. Although the Alliance Tech 5 study did include US06 data that should show the impact of oxygen on CO emissions from aggressive driving, the US06 data has not yet been made public. Therefore, for the present case the reductions for Tech 5 based on the Alliance study will be used <u>without</u> this extra 2.8 factor.

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[4] This value of 5.93333 can be found in the final version of the Predictive Model (16 June, 2000) at cell D21 of worksheet D.

[5] The Alliance, AIAM, Honda, "Industry Low Sulfur Test Program", presented at ARB Workshop, 7/2001. Available at http://www.arb.ca.gov/fuels/gasoline/meeting/2001/071201AAPrstn.pdf. and at http://www.autoalliance.org/archives/000125.html.

Recently the CRC-67 study has been released that used very new vehicles and several T-50, T-90, and ethanol levels. The analyses presented in the CRC-67 study are still under review, but some non-linearities do seem apparent with fuel oxygen and CO reduction. Contrary to the California's previous assumptions that the CO response would be greater above 2 weight percent, the study appears to show less response above 2 weight percent fuel oxygen. For the present analysis we will use the low T-50 results and the average of the zero to 2 weight oxygen response and the response from zero to 3.5 weight oxygen. Actually, such an average gives 7.1 percent CO reduction per percent fuel oxygen, which is close to the Alliance results of 7.5 percent CO reduction noted above. The average of the Alliance and CRC-67 studies is then 7.3 percent.

In order to use the averaged Alliance, 2001, and CRC-67, 2006, data to update the old 5.933 oxygen response we will go back again to Table 3 of ARB's 1999 Appendix G (page G2 below). That document shows that CO emissions in 2005 were then estimated to be 2071 tons per day from Tech 5. A 7.3 percent reduction of these (instead of zero) would have been 151.2 tons per day. When added to the old Table 5 total reduction of 296.44 tons, the new total would then be 447.6 tons reduced, which compared to the total emissions of 4995 given in Table 3 would then imply a "corrected" CO reduction rate of 8.96 percent per fuel oxygen percent. Thus, the implied CO reduction from non-oxy fuel to flatline fuel at 2 weight percent oxygen would be 17.9 percent. However, in the CaRFG3 regulations flatline fuel at 2 weight percent oxygen, is considered the base fuel, which then implies that non-oxy fuels would show an increase in CO of 21.8 percent compared to a flatline CaRFG fuel.

<u>The tons of CO (and equivalent VOC) reduced by E10</u> -- The total Statewide CO emissions for 2005 are estimated to be 7243 tons per day as taken from the ARB emissions report site[6]. It is reasonable to assume that this total would be for flatline CaRFG3, so non-oxygenated, as just noted, would be 21.8 percent higher or 8822 tons per day. Since the revised Predictive Model reduction factor would be 8.96 CO reduction per oxygen percent, then E10 with 3.5 percent oxygen would reduced CO by 31.4 percent. Such a reduction would amount to 2770 tons of CO reduced per day compared to using non-oxygenated CaRFG3. For 23.9 million vehicles this amounts to 105 grams per vehicle per day (including a 0.907 factor converting metric tons to U.S. tons). Using the recent ARB reactivity ratio of 0.026 between CO and exhaust VOC leads to an (on-road) offset of 72 tons of VOC per day Statewide (or 2.7 grams per day per vehicle). For E5.7 the tons offset would be 1579 tons Statewide using a linear relationship, which would be 60 grams per vehicle.

<u>Non-road use of gasolines</u> – In the 2005 ARB Draft Report of February on ethanol, their analysis of permeation impacts includes non-road emissions. Yet in the analysis of potential off-sets related to CO, non-road CO emissions are ignored. The U.S. EPA recommends (EPA, 2002) that oxygenated gasoline fuel can reduce non-road CO emissions by about 6.5 percent per fuel oxygen weight percent. The latest ARB gasoline statewide non-road CO inventory for summer 2005 is 2823 tons per day. If 2-weight

[6] http://www.arb.ca.gov/ei/emsmain/reportform.htm. Assumptions given were: statewide, summer, grown and controlled, on-road total – any diesel.

percent oxygen flatline is the base then the non-oxygenated non-road emissions would be nearly 15 percent higher or a total of 3245 tons CO. For E10 with 3.5 oxygen by weight the EPA-recommended CO reduction would amount to about 22.5 percent which would be 730 tons of non-road CO reduced per day. Using the recent ARB reactivity ratio of 0.026 between CO and exhaust VOC leads to a non-road offset of about 19 tons of VOC per day Statewide. Combined with the on-road estimate of 72 tons this gives and overall exhaust VOC equivalent offset through CO reduction of over 90 tons per day.

The NOx Issue

Another issue has been predicted NOx increases in the existing Predictive Model (PM) as fuel oxygen goes above the flatline 2 weight percent (which is E5.7). The Current PM shows an increase in NOx of 4.6 if fuel oxygen is increased from 2 weight percent to 3.5 percent (i.e. the amount in E10) and all other properties are held at the flatline values. This is roughly equivalent to assuming that 10 volume of ethanol can replace 11 percent volume of MTBE. At equal volumes the octane and many other parameters (i.e. T50, T90, aromatics, olefins, and sulfur) need not be different. Of course, some low boiling compounds such as isopentane must be removed to compensate for ethanol's RVP impact. Without this dramatic NOx increase it would have been almost as easy for refiners to use ethanol instead of MTBE at roughly equal volumes to make compliant CaRFG3. Instead, due to this NOx issue, for the last several years it was very difficult for refiners to use more than the flatline oxygen level corresponding to E5.7. In order to compensate for the predicted NOx increase in the PM, refiners would need to reduce olefins to near 1 percent and sulfur to near 1 ppm, which would severely limit the available feedstock for blending with ethanol not to mention the extra costs involved.

In early August, 2005, Cohen and Whitten made a presentation available at http://www.arb.ca.gov/fuels/gasoline/meeting/2005/mtg2005.htm. They showed for the main 7000 point database, which are for vehicles of model year 1986 to 1993 (Tech 4) the existing PM does not fit the data as well as a formulation using a duel model approach. Moreover, this type of approach appears to relate better to the overall NOx emissions in California. Remote sensing and the ARB emissions model EMFAC indicate that roughly 80 percent of the NOx emissions can be coming from only 20 percent of the vehicles. And in the Tech 4 database roughly 80 percent of the datapoints come from the lowest-emitting vehicles. That is, there appears to be an "80/20—20/80" mismatch problem in emissions levels between the real-world vehicle population and the database population. Cohen and Whitten used two distinctly different ways to address this "80/20" problem: one method weighted to data points by emissions contribution as used in EMFAC; the other used two models, one for moderate-plus vehicles (the 20 of the database emitting above certification levels) and the other model for the normal emitting vehicles (the 80 percent of the database emitting below the certification standard). The latter method offered the ability to test the approach against the data and it was found the such an approach fit the data very significantly better than the existing PM single-model type of approach. Both the weighted-data and the dual-model approach provide similar (near zero) NOx response to fuel oxygen. Hence, if either one of these approaches to dealing with the “80/20” problem are adapted, then refiners can easily blend ethanol up to the 10 percent limit.

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Attachment A

Appendix G

Carbon Monoxide Credit Estimation

from

Staff Report: Initial Statement of reasons, for the Proposed California Phase 3 Reformulated Gasoline Regulations

October, 1999

Appendix G
Estimation of a CO Credit

Effect of Fuel Properties on Light-Duty Vehicle Exhaust CO Emissions

The ARB staff evaluated the available data to investigate the effects of the various fuel properties on exhaust CO emissions. Data that were evaluated by ARB staff include results from the Auto Oil Air Quality Improvement Research program, the Coordinated Research Council Low Sulfur Study, the American Automotive Manufacturer Association's Sulfur Study, and the ARB's Ethanol Test Program. To determine the how each fuel parameter effects CO emission, we use a paired-data analysis in which we evaluated data for vehicles that was tested on fuels that only had different levels of one fuel property with the other fuel parameters as closely matched as possible. Based on the available data, the three properties that have the largest effect on CO emissions are; oxygen, sulfur, and T50.

Oxygen Effect On CO Emissions

Based on available emission test data, staff calculated the percent changes in CO emission per one weight percent change in oxygen content. Table 1 shows the reductions in CO emissions when oxygen content is increased, and Table 2 shows the increases in CO emissions when oxygen content is decreased. The data presented in Table and Table 2 are based on tests conducted using the Federal Test Procedure (FTP). The reductions for Federal Tier 1 and Advanced Vehicles were sufficiently small that they will be assumed to be zero. In U.S. EPA draft document, 'Fuel Oxygen Effects on Exhaust CO Emissions, Recommendations for MOBILE6,' March 16, 1998, the U.S.EPA also assumed that the effects of oxygen addition to be zero on CO emissions from these vehicle emission control technology groups.

To be consistent with the definitions for the vehicle classes used in the Predictive Model. Vehicles have been separated into the following groups: older vehicles (81 to 85 model years), Current vehicles (86 to 89 model years), Current vehicles (91 to 95 model years), Federal Tier 1 vehicles, and Advanced Technology vehicles. The older vehicles group (81 to 85 model years) are Tech 3 vehicles, Current vehicles (86 to 89 model years) and Current vehicles (91 to 95 model years) are Tech 4 vehicles, and Federal Tier 1 vehicles and Advanced Technology vehicles are Tech 5 vehicles.

Table 1. Summary of Percent CO Reduction Associated with a one percent Increased in Fuel Oxygen from Selected Studies

	Tech 3 Vehicles	Tech 4 Vehicles		Tech 5 Vehicles	
Study	81-86 MY	86 to 90 MY	91 to 95 MY	Federal Tier 1	Advance Tech.
Auto/Oil Bulletin #1	5.5%	4.7%	N/A	N/A	N/A
Auto/Oil Bulletin #4	6.1%	N/A	N/A	N/A	N/A
Auto/Oil Bulletin #6	N/A	5.0%	N/A	N/A	N/A
Auto/Oil Bulletin #17	N/A	5.4%	N/A	0.6%	-0.5%
ARB EtOH	N/A	N/A	1.39%	N/A	N/A
Average	5.8%	5.0%	1.39%	0.0%	0.0%

Table 2. Summary of Percent CO Increases Associated with a one percent Increased in Fuel Oxygen from Selected Studies

	Tech 3 Vehicles	Tech 4 Vehicles		Tech 5 Vehicles	
Study	81-86 MY	86 to 90 MY	91 to 95 MY	Federal Tier 1	Advance Tech.
Auto/Oil Bulletin #1	-4.5%	-5.2%	N/A	N/A	N/A
Auto/Oil Bulletin #4	-5.6%	N/A	N/A	N/A	N/A
Auto/Oil Bulletin #6	N/A	-4.3%	N/A	N/A	N/A
Auto/Oil Bulletin #17	N/A	-4.8%	N/A	-0.6%	0.5%
ARB EtOH	N/A	N/A	-1.35%	N/A	N/A
Average	-5.1%	-4.8%	-1.35%	0.0%	0.0%

CO Credit resulting From the Increase of Oxygen Content

For our calculations of emissions changes, EMFAC 7G was used to determine a baseline for CO emissions from the different groups of light-duty vehicles for the year 2005. The emissions for the different model year groups in the year 2005 are presented in Table 3.

Table 3. CO Emissions from Gasoline Vehicles

	81-85 MY	86 to 90 MY	91 to 95 MY	96 to 05 MY	Total
CO Emissions, TPD	712.00	1171.00	1041.00	2071.00	4995.00
Total Evaporative HC Emissions, TPD	22.48	43.67	69.67	59.23	195.05
Total Exhaust HC Emissions, TPD	58.80	86.50	116.20	104.40	365.90

It has been suggested that staff include effects of oxygen on off-cycle emissions of CO. Based on data from the ARB Ethanol study, it is estimated that the amount of reductions in CO emissions calculated as a weighted average using FTP and REPO5 test data is 2.8 times that of those calculated using FTP composite test data, alone. Given the lack of any other directly relevant information, this analysis will include percent changes in CO emissions determined from using FTP composite test data and those determined from using the weighted average of FTP and REPO5 emissions test data. The changes in CO emission when the fuel oxygen content is increased one weight percent are given in Table 4 and Table 5.

Table 4. Calculations of CO Reductions Based on FTP Composite Emissions

	81-85 MY	86 to 90 MY	91 to 95 MY	95 to 05 MY	Total
% CO Reduction per wt. % Oxygen	-5.07%	-4.76%	-1.35%	0.00%	
WT. % Oxygen Increased (1.0)	1.00	1.00	1.00	1.00	
Adjusted CO Reductions, TPD	-36.10	-55.72	-14.05	0.00	-105.87
Ozone Equivalent to CO Reductions, TPD	-2.53	-3.90	-0.98	0.00	-7.41
Eavp HC credit due to CO Reduction, TPD	1.10	1.70	0.43	0.00 4.9	3.22
Percent of Evap. HC Credit	4.89%	3.88%	0.61%	0.00%	1.65%
Exh. HC Credit due to CO Reduction, TPD	0.75	1.16	0.29	0.00	2.21
Percent of Exh. HC Credit	1.28%	1.35%	0.25%	0.00%	0.60%

Table5. Calculations of CO Reductions Base on FTP and REPO5 Emissions

	81-85 MY	86 to 90 MY	91 to 95 MY	95 to 05 MY	Total
% CO Reduction per wt. % Oxygen	-5.07%	-4.76%	-1.35%	0.00%	
WT. % Oxygen Increased (1.0)	1.00	1.00	1.00	1.00	
Weighted / FTP COMP	2.8	2.8	2.8	2.8	
Adjusted CO Reductions	-101.08	-156.01	-39.35	0.00	-296.44
Ozone Reduction from CO Reductions	-7.08	-10.92	-2.75	0.00	-20.75
Eavp HC credit from CO Reduction	3.08	4.75	1.20	0.00	9.02
Percent of Evap. HC Credit	13.68%	10.87%	1.72%	0.00%	4.63%
Exh. HC Credit from CO Reduction	2.11	3.26	0.82	0.00	6.19
Percent of Exh. HC Credit	3.59%	3.77%	0.71%	0.00%	1.69%

As shown in TABLE 4, the reduction in CO emissions for an increase of one weight percent in the oxygen content is estimated to be about 106 tons per day based on FTP composite emissions data. The MIR factor for CO is 0.07 grams of ozone per grams of CO; therefore the reduction in ozone that could be expected is about 7.42 tons per day. The average MIR factor for evaporative emissions has been calculated to be 2.21 gram of ozone per gram of VOC, therefore the evaporative emission equivalent to 7.42 tons of ozone is about 3.37 tons. The average MIR factor for exhaust emissions has been calculated to be 3.35, so the exhaust HC emissions equivalent is expected to be about 2.21 tons. This means that the CO reduction resulted from the increase of the oxygen content one weight percent could be used to offset about 1.7% of the total evaporative HC emissions. Similarly, the CO reductions could be used to offset about 0.56% of the total exhaust HC emissions.

From TABLE 5, the reductions in CO emissions are estimated to be about 296 tons per day based on the composite FTP and REPO5 data. Following the calculations described above, the reduction in ozone resulting from an increase of the oxygen content of gasoline by one is about 20.7 tons per day. Repeating the same calculations, it follows that the CO reduction resulting from the increase of the oxygen content could be used to offset about 4.8% of the total evaporative HC emissions. Similarly, the CO reductions could be used to offset about 1.6% of the total exhaust HC emissions. The HC emissions credit would be applied to the final predicted percent change in exhaust or evaporative emissions in the Predictive Model.

Table 6. VOC Adjustment Factors for Increase in Oxygen content by One Weight %

	FTP DATA	FTP And REPO5 Data
Evaporative HC Credit	-1.7%	-4.8%
Exhaust HC Credit	-0.56%	-1.6%

CO Debit Resulting form the Reduction in Oxygen

Reducing the oxygen content of a gasoline will result in an increase in CO and HC emissions. If a refiner removed the oxygen from a fuel meeting the flat limits, then exhaust hydrocarbon emissions would increase. Refiners will need to adjust other parameters of gasoline in order to offset the increase in HC emissions resulting from the reduction in oxygen content. Of the eight fuel properties that are regulated by the CaRFG2 regulations, the ones that are most likely to be adjusted to offset the increase in hydrocarbon emissions would be sulfur and T50. Both lowering the sulfur content and the T50 of gasoline will lower HC emissions. In addition, lowering the sulfur content and T50 will also reduce CO emissions; this would reduce the impact associated with reducing the oxygen content of gasoline.

Although limited, the data from the ARB Ethanol testing program supported the proposition that there exists a differential effect on CO emission associated with increasing oxygen on off-cycle emissions. The ARB Ethanol testing program did not test a zero oxygen fuel. Data are available from a 1996 ARB Mobile Source Division emissions factor test program, where several fuels were tested on both the FTP cycle and the Unified Cycle (LA92 Cycle). The Unified Cycle was developed to represent the average trip in the South Coast Air Quality Management District. Data from this study indicated that there are no significant difference in the CO emissions between the FTP cycle and the Unified Cycle (LA92 Cycle) when comparing a non-oxygenated gasoline with a gasoline containing 2 percent oxygen. While, the two fuels differed in other properties, for CO the most important factor is the oxygen content. For assessing the impact on CO emissions associated with going from a 2 percent oxygen fuel to a zero percent oxygen no off-cycle adjustment will be used in the analysis.

Table 6 shows the increase in CO emissions CO emission for one-percent reduction in the oxygen content of gasoline.

Table 7. CO Increases Due to the Reduction in Oxygen

	81-85 MY	86 to 90 MY	91 to 95 MY	95 to 05 MY	Total
% CO Increased per wt. % Oxygen Reduced	5.80%	4.99%	1.39%	0.00%	
WT. % Oxygen Increased (1%)	1.00	1.00	1.00	1.00	
Adjusted CO Increases, TPD	41.27	58.48	14.47	0.00	114.22
Ozone Increases Due to CO Increase, TPD	2.89	4.09	1.01	0.00	8.00
Eavp. HC Debit from CO Increase, TPD	1.26	1.78	0.44	0.00	3.48
Percent of Evap. HC Debit	5.59%	4.08%	0.63%	0.00%	1.78%
Exh. HC Credit from CO Increase, TPD	0.86	1.22	0.30	0.00	2.39
Percent of Exh. HC Debit	1.47%	1.41%	0.26%	0.00%	0.65%

From Table 7, the increase in CO emissions resulting from a reduction of oxygen content by one weight percent is 115 tons per day based on the composite FTP data. This increase in CO ozone equates to an increase in ozone of about 8.0 tons per day. The CO increase associated with reducing oxygen content could result in a HC debit about 1.8% of the total evaporative HC emissions or about 0.65% of the total exhaust HC emissions.

Table 8 presents an estimate of how reducing the sulfur content of gasoline could offset the CO emissions increase associated from reducing the oxygen content of gasoline. The amount of CO emissions reduced by reducing the sulfur content 10 parts per million (ppm) is about 47 tpd.

TABLE 8. Sulfur Effect on CO Emissions

	81-85 MY	86 to 90 MY	91 to 95 MY	95 to 05 MY	Total
% CO Reduced per10 PPM Sulfur Reduced	0.0%	-0.4%	-0.4%	-1.8%	-0.9%
Sulfur Reduction (10 ppm)	1	1	1	1	1
% CO Decreased from Sulfur Redcution	0.0%	-0.4%	-0.4%	-1.8%	-0.9%
CO Decreases from Sulfur Redcution,TPD	0.0	-4.4	-4.0	-38.2	-46.6
Ozone Change Due to CO Increase, TPD	0.00	-0.31	-0.28	-2.67	-3.26

Table 9 presents an estimate of how reducing the T50 of gasoline could offset the CO emissions increase resulting from reducing the oxygen content of gasoline. The amount of CO emissions reduced by reducing the T50 by 5 degrees is about 40 tpd.

TABLE 9: Effect of T50 Reduction on CO Emission

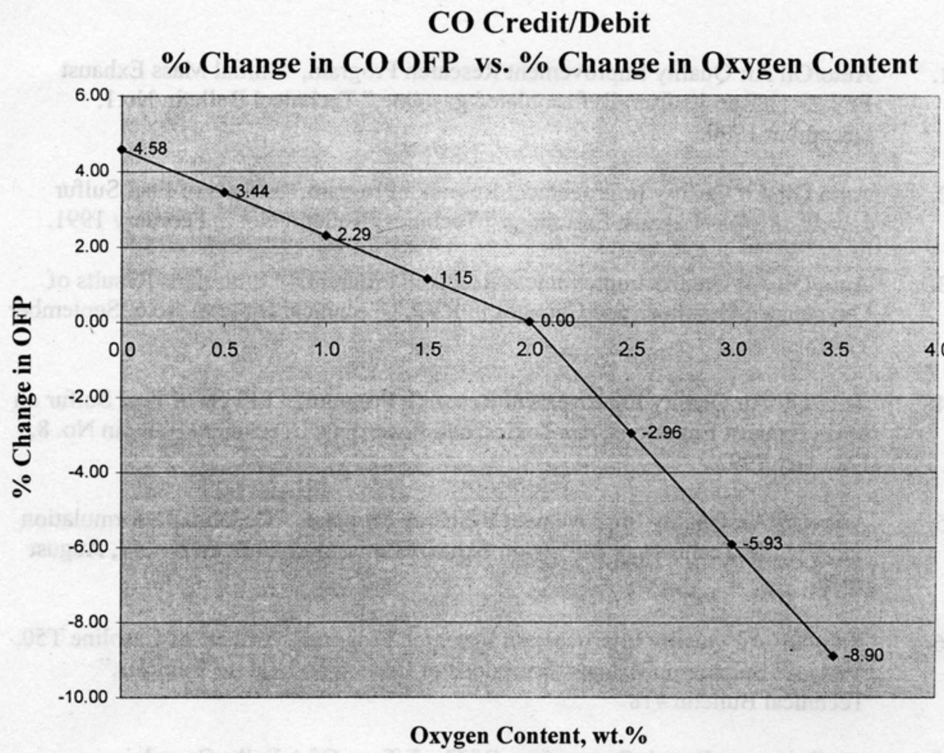
	81-85 MY	86 to 90 MY	91 to 95 MY	95 to 05 MY	Total
% CO Reduced per one degree T50 Reduced	-0.16%	-0.16%	-0.16%	-0.16%	-0.16%
T50 Reduction (5 dgrees)	5	5	5	5	5
% CO Decreased from T50 Redcution	-0.80%	-0.80%	-0.80%	-0.80%	-0.80%
CO Decreased from T50 Redcution, TPD	-5.7	-9.3	-8.3	-16.5	-39.8
Ozone Change Due to CO Increase, TPD	-0.4	-0.7	-0.6	-1.2	-2.8

Table 10 presents the expected change in CO emissions when oxygen content is decreased from 2.0% to 0%, sulfur content reduced by 10 ppm, and T50 reduced by 5 °F. A 9.9-tpd increase in ozone equates to about 4.5 tpd of evaporative emissions. This calculates to about 2.3 percent increase in evaporative HC emissions.

The flat limit for RVP in the proposed CaRFG3 specifications is 7.0 psi. Based on the proposed CaRFG3 Predictive Model the 6.9 baseline for using the evaporative hydrocarbon emissions model the 0.1 psi reduction in RVP would be expected to reduce emissions of evaporative hydrocarbons by about 3.4 percent. Therefore the effect on CO associated with a removing oxygen from a fuel complying with the proposed CaRFG3 specifications is significantly less than effect on emission from a 0.1 psi reduction in RVP.

Table 10. Expected Change in Emissions

	Change in CO, tpd	Expected Change in Ozone, tpd.	Change in Evaporative HC, tpd	Percent Change in Total Evaporative HC
Reducing Oxygen by 2 weight percent	228.4	16.0	7.2	3.7%
Reducing Sulfur by 10 ppmw	-46.6	-3.3	-1.5	-0.8%
Reducing T50 by 5 °F	-39.8	-2.8	-1.3	-0.7%
Total	142.0	9.9	4.5	2.3%


CO Credit/Debit
% Change in CO OFP vs. % Change in Oxygen Content
% Change in OFP
Oxygen Content, wt.%
6.00
4.00
2.00
0.00
-2.00
-4.00
-6.00
-8.00
-10.00
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.58
3.44
2.29
1.15
0.00
-2.96
-5.93
-8.90

References to Example of CO Credit Calculations

1. Auto/Oil Air Quality Improvement Research Program, "Initial Mass Exhaust Emissions Results from Reformulated gasoline," Technical Bulletin No.1, December 1990.

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5. Auto/Oil Air Quality Improvement Research Program, "Gasoline Reformulation and Vehicle Technology Effects on Exhaust Emission," Bulletin No. 17, August 1995.

6. Auto/Oil Air Quality Improvement Research Program, "Effects of Gasoline T50, T90, and Sulphur on Exhaust Emissions of Current and Future Vehicles," Technical Bulletin #18

7. Air Resources Board, Comparison Of The Effects Of A Fully-Complying Gasoline Blend And A High RVP Ethanol Gasoline Blend On Exhaust And Evaporative Emissions, November 1998

8. Results from the American Automobile Manufacturers Association's Sulfur Study

9. Results from the Coordinated Research Council's Sulfur Study